Sleuthing Clandestine Chemistry

As the 'criminal chemists' become more sophisticated in their technique, so too must the 'analytical detectives' — the forensic chemists

BY LINDA GARMON

"Crime is common. Logic is rare. Therefore it is upon the logic rather than upon the crime that you should dwell."
— Sherlock Holmes in *The Adventure of the Copper Beeches* by Sir Arthur Conan Doyle

If novelists intend to dream up new exploits of Sherlock Holmes, they should not overlook a chemical theme.

Consider, for example, the following plot: An alleged textile and dye company purchases a quantity of acetic anhydride. It then purchases about 2,000 pounds of anthranilic acid. Because government agents suspect the company is illegally manufacturing a controlled drug substance, they call in a special detective who explains that the anhydride can be used to convert the acid into a precursor of the depressant methaqualone (Quaalude), a controlled drug substance. In order to convert the precursor to methaqualone, however, the company needs one of three additional chemicals — A, B or C.

Government agents continue their surveillance of the operation, but no A, B or C is purchased. Instead, the company acquires nine 55-gallon drums of o-chloroanaline. Again, the agents consult the detective, who turns to the journals of chemistry. Finally, he lays his finger on the solution to the mystery: The scientific literature documents that by substituting o-chloroanaline for chemical A, it is possible to produce mecloqualone, a controlled substance in the same chemical family as methaqualone.

Precisely. A search warrant is issued and the suspected clandestine operation is seized.

But the detective in this story returns to a laboratory, rather than to 221B Baker St.; his faithful friend is a mass spectrometer, not Dr. Watson; and his story cannot be placed among volumes of fiction. This modern-day Sherlock is a forensic chemist and the solution to his case was far from elementary.

In fact, the solution turned out to be somewhat more complicated than the initial mecloqualone explanation. Most of the known syntheses of mecloqualone require the use of either a condensing agent — an extra chemical needed to make the reaction go — or special equipment. But the authorities found neither condensing agent nor special equipment in the seized laboratory; so it was up to the forensic chemist to determine whether special conditions were enough to produce the controlled drug. When the chemist discovered that merely heating the reaction and adding an excess amount of one of the chemicals made the reaction go, sufficient scientific evidence was present for successful prosecution of the criminal chemists, preventing a potential 2.7 million mecloqualone tablets from entering the illicit drug market.

The mecloqualone mystery — reported in the June ANALYTICAL CHEMISTRY by Richard S. Frank and colleagues of the Drug Enforcement Administration (DEA) — demonstrates that forensic chemists need to keep abreast of alternative synthetic schemes.

DEA agents depend, to a large extent, on the Clandestine Laboratory Guide — a sort of drug-enforcement bible compiled by forensic chemists — to identify suspected clandestine operations. This guide not only lists different recipes for controlled drugs, but also cross-references recipe ingredients. The cross-reference portion often enables DEA agents to guess what a suspect laboratory is synthesizing merely by monitoring the chemicals the laboratory purchases. For example, the purchase of alcohol, benzene, chloroform, lithium hydroxide and 11 other specific chemicals flags potential LSD synthesis, according to the laboratory guide.

But the avenues of synthesis listed in even the most recent edition of the laboratory guide soon become obsolete, because the clandestine operators constantly are introducing slight changes to the controlled drug recipes. "If they [clandestine operators] can find another chemical that is not on our list but will do the same job, they figure they can circumvent any enforcement activity we may have," explains DEA chemist Mike Leser. "So we're constantly looking for things [chemicals or special equipment or conditions] that can be substituted in place of a chemical but that gives the same results."

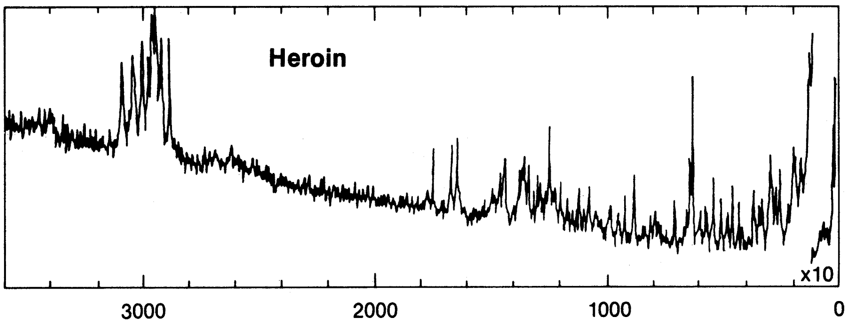
When employed by the clandestine community, the art of substitute synthesis leads to some fairly complex chemical schemes for the forensic chemist to unravel. Ironically, the job of DEA chemists sometimes is further complicated by DEA's own prized legal possession — the Controlled Substances Act. The Act requires persons who handle controlled substances to obtain registrations issued by DEA. Although most controlled substances are the synthetic end products — such as narcotics, depressants and stimulants —

A trace of evidence

Unidentified substances recovered from seized clandestine laboratories sometimes are "in very small quantities — residues on a beaker or stirring rod, for example," says forensic chemist Marc Cunningham. The development of highly sensitive analytical tools to identify these trace amounts of "unknowns" is of great interest to forensic chemists.

One trace detector that has potential forensic application, says John Blaha of the National Bureau of Standards, is the Raman microprobe. Developed by NBS researchers, this technique recently has been used to identify the presence of a number of controlled drugs in micrometer-size particles of 1-to-10-picogram masses.

In the Raman instrument, single particles of a substance are moved into the path of a laser beam. The light scattered by the sample contains the Raman spectrum of the particle, which indicates characteristic molecular and crystalline vibrations of the sample. This structural activity is indicated, for example, by the greater number and intensity of bands in the carbon-hydrogen stretching region near 3,000 cm^{-1} on the heroin spectrum.



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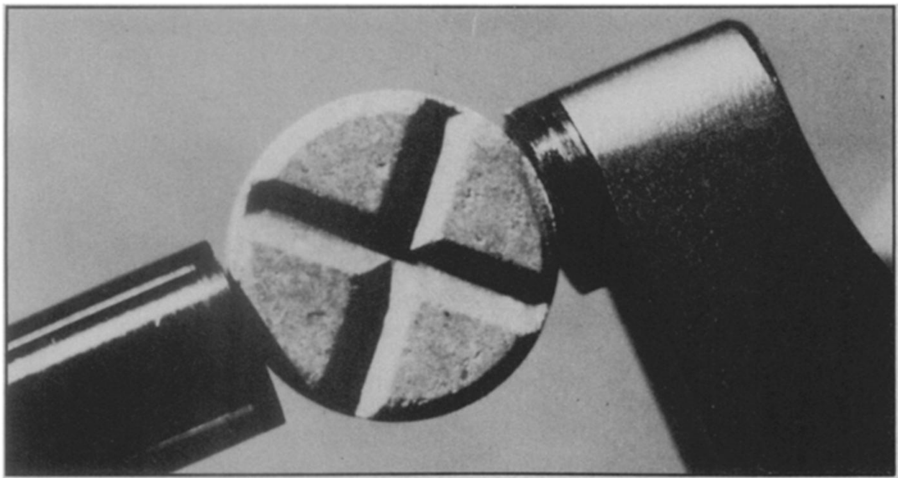
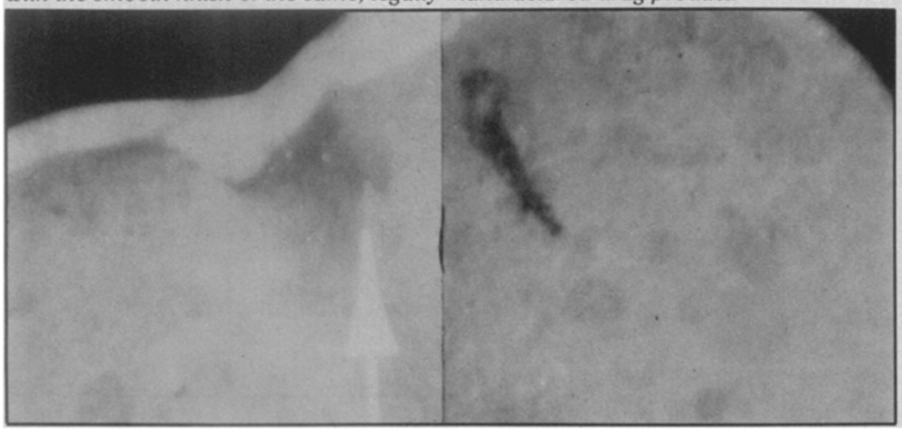
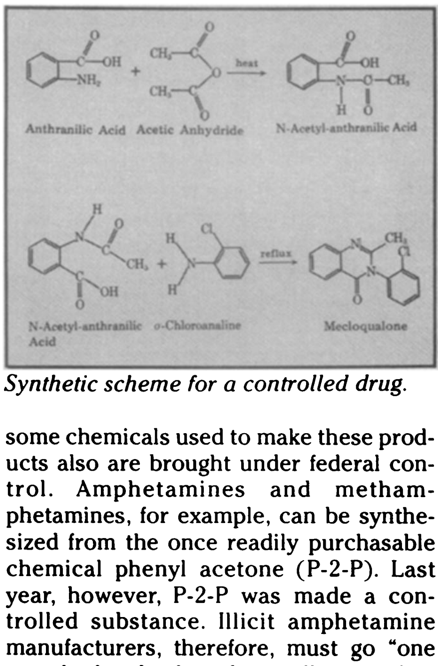

DEA

Evidence of illicit manufacture: A telltale diameter (above) and a rough edge compared with the smooth finish of the same, legally manufactured drug product.





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Synthetic scheme for a controlled drug.

some chemicals used to make these products also are brought under federal control. Amphetamines and methamphetamines, for example, can be synthesized from the once readily purchasable chemical phenyl acetone (P-2-P). Last year, however, P-2-P was made a controlled substance. Illicit amphetamine manufacturers, therefore, must go "one step farther back and actually manufacture the phenyl acetone," Leser says. "It's a little bit more sophisticated now than the normal one-step operation." And it becomes a more sophisticated puzzle for the forensic chemist.

In addition to piecing together the precise chemical scheme a suspected clandestine operation is using, the forensic chemist is expected to be able to pinpoint precisely where the manufacturers are on the scheme — whether they have only starting materials, intermediaries or final product. The task requires a lot of "sitting on the outside, trying to figure out what they're doing on the inside," explains one DEA investigator. This means noting everything from late working hours and discarded materials to as seemingly innocent an activity as going to the corner store to buy ice.

But activities that can be observed only "on the outside" are easily subject to misinterpretation, which sometimes results in a laboratory raid prior to the time of the finished product. "There was one instance where we had a suspect lab go down in West Virginia," Leser says, "prior to the actual manufacture [of, in this case, methamphetamine]. The gentleman had purchased his chemicals and glassware... and had exhibited activity which was characteristic of actual manufacture." Upon seizure of the laboratory, however, chemists discovered that the man was "just at the beginning stages; he hadn't actually done any cooking," Leser says. In such cases, the clandestine operator is charged with intent to manufacture a controlled substance, and the forensic chemists must prove in court that the operator had the capability to synthesize that substance.

Even when the timing is right, though, and a laboratory is raided post finished product, investigators may be in for another chemical surprise. In one case, "A substance came in which was purported to be a clandestine lab manufacture," says DEA chemist Marc Cunningham. Although the substance tested positively in color analyses — in which chemicals are added to the "unknown" to see if it turns a characteristic color — another analytical tool seemed to indicate that the substance was either totally contaminated or an altogether different substance. After carefully studying the analytical test results, Cunningham discovered that the suspect substance was, in fact, an isomer of the controlled substance — it had the same kinds and numbers of atoms but a different structural orientation of those atoms — and was not under federal control. Failure to identify it as such would have resulted not only in some red-faced investigators, but also in several false arrests.

Although forensic chemists have several analytical tools of the trade, they most often rely on the gas chromatograph/mass spectrometer (GC/MS) for identification of "unknowns." Mass spectrometers identify the mass-to-charge ratio of fragments generated by the instrument. The fragments can be generated either by bombarding the "unknown" with electrons (electron-impact mass spectrometer) or by placing it in a magnetic field (quadropole mass spectrometer). In either method, the instrument prints out a mass spectrum—a plot of intensity versus mass of the fragments. "Unknowns" are identified by characteristic peaks on the mass spectrum printout.

Interestingly, even these "characteristic peaks" once were the subject of debate in a court case involving an alleged clandestine methamphetamine laboratory. "During jury trial, the defense [representing the suspect clandestine operators] introduced the argument that the DEA, having used a GC/MS for identification of the methamphetamine, failed to prove beyond reasonable doubt that the substance was methamphetamine," writes chemist Frank in his ANALYTICAL CHEMISTRY report. "Defense introduced literature stating that quadropole mass spectrometry cannot resolve the difference between methamphetamine and phentermine [a noncontrolled drug substance]." In response to the highly technical defense, the forensic chemist involved in the case presented a "graphic explanation of peak ratio calculations" to demonstrate that the sample was methamphetamine.

Although Frank remembers that the court accepted the forensic chemist's explanation of peak ratio calculations, he does not recall the outcome of the case. "That is not significant to forensic science," he says. "We are not there to win or lose; we are merely there to present facts and to support the facts that we found."

Apparently, it is upon the logic rather than upon the crime that the forensic chemist dwells. □